

# Formation and chemistry of the transient 17-electron compounds $\text{CpFe}(\text{CO})\text{L}^\cdot$ ( $\text{L} = \text{PMe}_2\text{Ph}, \text{PPh}_3$ )

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## Abstract

Hydride hydrogen atom abstraction from the 18-electron compounds  $\text{CpFe}(\text{CO})\text{LH}$  ( $\text{L} = \text{PMe}_2\text{Ph}, \text{PPh}_3$ ) by the trityl radical results in formation of the 17-electron species  $\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})^\cdot$  and  $(\text{CpFe}(\text{CO})\text{PPh}_3)^\cdot$ . These compounds are not stable, however, undergoing rearrangement and coupling reactions to give, ultimately, the 18-electron compounds  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PMe}_2\text{Ph}$  and  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$ , respectively. The transient, 17-electron species may be trapped by organic halides  $\text{RX}$ , which transfer halogen atoms to give the compounds  $\text{CpFe}(\text{CO})\text{LX}$ .

**Keywords:** Iron; 17-Electrons; Radicals

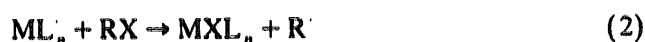
## 1. Introduction

The distinct and diverse chemistry of 17-electron, metal-centered radicals continues to be of interest, as reports of syntheses of persistent radicals and investigations of their often characteristic chemical properties continue to appear [1]. Indeed, 17-electron compounds may be synthesized in a variety of ways [1], and are often stabilized with respect to dimerization to the 18-electron, metal–metal bonded analogs by substitution of small ligands by more sterically demanding ligands (e.g. CO by tertiary phosphines) [2]. As part of the development of methodologies for the syntheses of novel 17-electron species, we [3–5] and others [6–10] have demonstrated the utility of persistent triarylmethyl radicals  $\text{Ar}_3\text{C}^\cdot$  to abstract hydrogen atoms from 18-electron, transition metal hydride complexes  $\text{MHL}_n$  and form the corresponding 17-electron compounds  $\text{ML}_n^\cdot$  (Eq. (1)).



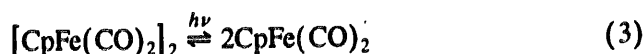
In the absence of suitable radical traps, the species  $\text{ML}_n^\cdot$  may couple and the organometallic products obtained are often the 18-electron, metal–metal bonded dimers  $[\text{ML}_n]_2$ . Transient species may also be identified

by trapping experiments, of which halogen abstraction reactions from organic halides have been found to be particularly useful (Eq. (2)) [3,11].



However, in those cases where radical coupling is not feasible for steric reasons, the chemistry of Eq. (1) provides a very convenient route to new 17-electron compounds which may be isolated if dimerization is precluded by coordination of appropriately bulky ligands.

As part of a general program to gain better understanding of the factors governing stabilities of 17-electron complexes, we have been attempting to prepare persistent, 17-electron compounds of the type  $\eta^5\text{-Cp}'\text{Fe}(\text{CO})\text{L}^\cdot$  ( $\text{Cp}' = \text{Cp}$ , substituted Cp;  $\text{L} =$  bulky phosphines) [4,12,13]. These are analogs of the very unstable species  $\text{CpFe}(\text{CO})_2^\cdot$ , which has been generated photochemically from the corresponding dimer but which is exceedingly reactive and recombines rapidly to form the corresponding 18-electron dimer (Eq. (3)) [14,15].



In attempts to prepare derivatives of  $\text{CpFe}(\text{CO})_2^\cdot$ , we have met with some success by employing pentaaryl-cyclopentadienyl ligands, and have demonstrated that the

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18-electron compounds  $[\eta^5\text{-C}_5\text{Ph}_5\text{Fe}(\text{CO})_2]_2$  and  $[\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\text{Fe}(\text{CO})_2]_2$  dissociate spontaneously in solution at ambient temperature to give measurable concentrations of the corresponding 17-electron monomers [4,13]. A complementary approach would be to employ sterically more demanding tertiary phosphine ligands and, as the di-iron compound  $[\text{CpFe}(\text{CO})(\text{PPh}_3)]_2$ , for instance, cannot be made directly from  $[\text{CpFe}(\text{CO})_2]_2$  and  $\text{PPh}_3$  [16,17], it was anticipated that  $\text{CpFe}(\text{CO})\text{PPh}_3$  would be too sterically encumbered to dimerize if formed via hydrogen atom abstraction as in Eq. (4).



$\text{L} = \text{PMe}_2\text{Ph}, \text{PPh}_3$

We now discuss experiments which show that the 17-electron compounds  $\text{CpFe}(\text{CO})\text{L}^\cdot$  ( $\text{L} = \text{PPh}_3$  (A)  $\text{PMe}_2\text{Ph}$  (B)) may readily be formed from the corresponding hydrides  $\text{CpFe}(\text{CO})\text{LH}$  (Eq. (4)), but only as transients en route to the di-iron compounds  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{L}$ . Aspects of this work have been reported [4].

## 2. Experimental

Experiments were conducted under an inert atmosphere of oxygen-free nitrogen, further purified through columns containing heated BASF catalyst and molecular sieves. Manipulations of air-sensitive materials followed standard Schlenk line techniques and included the use of a Vacuum Atmospheres Glove Box. The solvents benzene, toluene, tetrahydrofuran, hexanes and diethyl ether were dried and distilled over alkali metals.  $\text{CH}_2\text{Cl}_2$  was dried and distilled over  $\text{CaH}_2$ . Solvents were thoroughly deoxygenated prior to use by saturation with  $\text{N}_2$  or repeated freeze-thaw cycles. Chromato-

graphic separations were typically carried out in a cold-water jacketed column using alumina or silica gel. Chemicals were obtained from Aldrich, BDH, Fischer, Strem and Fluka and were used as-received.

IR spectra were acquired on Bruker 85 IFS FT-IR and Bruker IFS 25 FT-IR spectrometers; IR data are presented in Table 1. NMR spectra were run on Bruker ACF 200 (200.1 MHz  $^1\text{H}$ , 50.3 MHz  $^{13}\text{C}\{^1\text{H}\}$ ) and AM 400 (400.1 MHz  $^1\text{H}$ , 100.6 MHz  $^{13}\text{C}\{^1\text{H}\}$ ) NMR spectrometers. The residual proton and the carbon resonances of deuterated solvents served as internal references for  $^1\text{H}$  and  $^{13}\text{C}$  resonances respectively.  $^{31}\text{P}$  NMR spectra were run on an AM 400 (162 MHz) NMR spectrometer, and were referenced to external 85%  $\text{H}_3\text{PO}_4$ . Elemental analyses for carbon and hydrogen were carried out by Canadian Microanalytical Services, Delta, British Columbia.

Solutions containing the trityl dimer–monomer equilibrium were prepared by the zinc reduction of  $\text{Ph}_3\text{CCl}$  [3–10] in benzene, and all syntheses and manipulations involving trityl radical-dimer were conducted in the absence of light.  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$  and  $\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})\text{H}$  were prepared via procedures reported previously for the latter [18]. The yellow, solid  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$  was characterized spectroscopically.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.65 (m, 6H, Ph), 7.02 (m, 9H, Ph), 4.26 (s, 5H, Cp),  $-12.8$  (d,  $J_{\text{PH}} = 78.9$  Hz, 1H, Fe–H) [19–21]. IR (benzene):  $\nu_{\text{CO}}$  1925  $\text{cm}^{-1}$ . The compound  $\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})\text{H}$  was isolated as an oil and characterized spectroscopically [18–21].  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.49–7.42 (m, 2H, Ph), 7.14–7.01 (m, 4H, Ph), 4.20 (s, 5H, Cp), 1.29 (d,  $J_{\text{PH}} = 2.9$  Hz, 3H, PMe), 1.27 (d,  $J_{\text{PH}} = 2.8$  Hz, 3H, PMe),  $-13.91$  (d,  $J_{\text{PH}} = 79.6$  Hz, 1H, Fe–H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  220.9 (d,  $J_{\text{PC}} = 28$  Hz, CO), 142.5 (d,  $J_{\text{PC}} = 37$ , *ipso*-C, aryl), 130.1 (d,  $J_{\text{PC}} = 10$  Hz, Ph), 129.1 (Ph), 128.3 (Ph, second resonance partially obscured by solvent resonances), 79.3 (Cp C).

Table 1  
IR and  $^1\text{H}$  NMR data

Compound	$\nu_{\text{CO}}$ ( $\text{cm}^{-1}$ )	$^1\text{H}$ Chemical Shifts ( $\delta$ )
$\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$	1925 (benzene), 1930, 1885 (Nujol)	4.26 (s, Cp), $-12.8$ (d, $J_{\text{PH}} = 78.9$ Hz, Fe–H)
$\text{CpFe}(\text{CO})(\text{PPh}_3)\text{Cl}$	1959 ( $\text{CH}_2\text{Cl}_2$ ), 1958 ( $\text{CCl}_4$ )	4.13 (s, Cp)
$\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$	1950 (br.s), 1772 (w), 1723 (s) ( $\text{CH}_2\text{Cl}_2$ ) 1953 (m), 1929 (m), 1731 (s) (benzene)	4.22 (s, Cp)
$\text{CpFe}(\text{CO})_2\text{H}$	2015, $\sim 1960$ (benzene)	
$\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})\text{H}$	1914, 1875 sh (benzene) 1930, 1885 sh (Nujol)	4.20 (s, Cp), 1.29 (d, $J_{\text{PH}} = 2.9$ Hz, PMe), 1.27 (d, $J_{\text{PH}} = 2.8$ Hz, P–Me), $-13.91$ (d, $J_{\text{PH}} = 79.6$ Hz, Fe–H)
$\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})\text{Cl}$	1952 (benzene), 1956 ( $\text{CCl}_4$ ), 1952 ( <i>n</i> -BuCl)	
$\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})\text{Br}$	1946 (benzene)	3.99 (s, Cp), 1.69 (d, $J_{\text{PH}} = 10.4$ Hz, PMe), 1.35 (d, $J_{\text{PH}} = 9.6$ Hz, PMe)
$\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})\text{I}$	1943 (benzene)	3.94 (s, Cp), 1.73 (d, $J_{\text{PH}} = 10$ Hz, PMe), 1.43 (d, $J_{\text{PH}} = 9.2$ Hz, PMe)
$\text{CpFe}(\text{CO})_2\text{Cl}$	2036, 1996 (benzene)	
$\text{CpFe}(\text{CO})_2\text{I}$	2043, 2000 ( $\text{CHCl}_3$ )	

22.3 (d,  $J_{PC}$  16 Hz, PMe), 21.9 (d,  $J_{PC}$  15 Hz, PMe). IR (benzene): 1917, 1873  $\text{cm}^{-1}$  (sh).

### 2.1. Hydrogen atom abstraction reactions of $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$

A trityl solution was generated by the reaction of 1.56 g ( $2.39 \times 10^{-2}$  mol) Zn and 2.01 g ( $7.21 \times 10^{-3}$  mol)  $\text{Ph}_3\text{CCl}$  in 90 ml benzene over 18 h, and 60 ml of this solution were added to a yellow solution of 0.51 g ( $1.24 \times 10^{-3}$  mol)  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$  in 20 ml benzene. After 30 min, the reaction vessel was placed in an ice bath and stirring was continued for 60 min as the solution turned dark green. IR bands were observed at 1912 (m) and 1732  $\text{cm}^{-1}$  (m). The solvent was then removed in vacuo, the residue was redissolved in 10 ml of toluene and transferred to a water-jacketed ( $T \leq 284\text{K}$ ) chromatographic column packed with silica gel and equilibrated with hexanes. A yellow band containing trityl materials was eluted with a toluene–hexanes solution (2:1 v/v), a green band with pure toluene. The latter eluate was collected in a flask cooled in an ice bath, the solvent was removed in vacuo and the dried solid was identified as the known  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$  [16,17,22,23]. Yield 48%. IR ( $\text{CH}_2\text{Cl}_2$ ): 1950 (br,s), 1772 (w), 1723  $\text{cm}^{-1}$  (s); lit. (benzene): 1950, 1930, 1732  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  ca. 4.22 (br, Cp). A second green band, containing  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{Cl}$ , was eluted with THF. IR ( $\text{CH}_2\text{Cl}_2$ ): 1959  $\text{cm}^{-1}$ ; lit. 1960  $\text{cm}^{-1}$  [16,24]. Confirmation of this assignment was made by the synthesis of  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{Cl}$  through the reaction of  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$  with  $\text{CCl}_4$  [16], yielding the expected product with an IR band at 1958  $\text{cm}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ .

Black crystals of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$  [16,22,23] were also inadvertently obtained during synthesis of  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$ ; a dark green  $\text{CH}_2\text{Cl}_2$  solution of the product exhibited IR bands at 1948 (br,s), 1764 (w) and 1723  $\text{cm}^{-1}$  (s). In benzene, bands were observed at 1953 (m), 1929 (m) and 1731  $\text{cm}^{-1}$  (s). Elemental analyses of the compound with half a mole of hexane were satisfactory. Anal. Found: C, 64.11; H, 4.30.  $\text{C}_{34}\text{H}_{32}\text{Fe}_2\text{O}_3\text{P}$ . Calc.: C, 64.69; H, 4.57%.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.83 (m, Ph), 7.06–6.93 (m, Ph), 4.21 (br, Cp). Hexanes resonances were present at  $\delta$  1.25 (br, m), 0.88 (t).

For purposes of comparison,  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$  was also prepared, as described in the literature, by refluxing a solution of  $\text{Cp}_2\text{Fe}_2(\text{CO})_4$  and  $\text{PPh}_3$  in benzene [16,17]. The  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$  derived in this way was identical (IR,  $^1\text{H}$  NMR) to the materials described above. IR ( $\text{CH}_2\text{Cl}_2$ ): 1948 (br), 1768 (w), 1723  $\text{cm}^{-1}$  (s).

#### 2.1.1. Reaction of $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$ with trityl in the presence of $\text{Ph}_3\text{CCl}$

A mixture of 1.39 g ( $4.99 \times 10^{-3}$  mol)  $\text{Ph}_3\text{CCl}$  and 1.05 g ( $1.61 \times 10^{-2}$  mol) Zn in benzene was stirred for

19 h, and then filtered into a flask containing 0.35 g ( $1.26 \times 10^{-3}$  mol)  $\text{Ph}_3\text{CCl}$ . A solution of 0.50 g ( $1.21 \times 10^{-3}$  mol)  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$  in 10 ml benzene was then added, and the mixture was stirred for 5.5 h. The solvent was removed from the mossy-green solution, and  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{Cl}$  was established as the major product present. IR ( $\text{CH}_2\text{Cl}_2$ ): 1958  $\text{cm}^{-1}$  [24].  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  4.13 (s, Cp).

#### 2.1.2. Reaction of $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$ and $\text{Ph}_3\text{CCl}$

A solution of 0.050 g ( $1.21 \times 10^{-4}$  mol)  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$ , in 10 ml of benzene was treated with 0.036 g ( $1.29 \times 10^{-4}$  mol)  $\text{Ph}_3\text{CCl}$ . After 80 min, the solution was still yellow and the CO band in the IR spectrum of the hydride was observed at 1924  $\text{cm}^{-1}$ . After 2 h, the solution was greenish yellow, the CO band at 1924  $\text{cm}^{-1}$  had decreased in intensity and new bands were present at 2049 (w), 2003 (w), 1952 (s) and 1716  $\text{cm}^{-1}$ . No starting material was present after 4.5 h, and the IR spectrum of the now green solution exhibited CO bands at 2036 (br,w), 1996 (br,w),  $\sim$ 1963 (sh) and 1952  $\text{cm}^{-1}$  (m).

#### 2.1.3. Reaction of $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$ and trityl dimer in $\text{CH}_2\text{Cl}_2$

A solution of 0.082 g ( $1.99 \times 10^{-4}$  mol)  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$  in 20 ml  $\text{CH}_2\text{Cl}_2$ , exhibiting a strong CO band in the IR spectrum at 1921  $\text{cm}^{-1}$ , was cannulated onto 0.261 g ( $5.36 \times 10^{-4}$  mol) trityl dimer in a separate flask. Immediately after addition, an IR spectrum exhibited a strong band at 1959  $\text{cm}^{-1}$  and showed that the band at 1921  $\text{cm}^{-1}$  had decreased significantly. The reaction mixture was then cooled in an ice bath and, after 3 h, there was observed a strong band at 1960  $\text{cm}^{-1}$ , attributable to  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{Cl}$  [24], but no bands attributable to either  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$  or  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$ .

#### 2.1.4. Reaction of $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$ with trityl in the presence of $\text{PMe}_2\text{Ph}$

A solution of 0.203 g ( $0.493 \times 10^{-3}$  mol)  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$  and 69  $\mu\text{l}$  ( $0.485 \times 10^{-3}$  mol)  $\text{PMe}_2\text{Ph}$  in 10 ml benzene, cooled in an ice bath, was treated with a solution of trityl in benzene. Within 11 min, an IR spectrum exhibited only a single band, at 1918  $\text{cm}^{-1}$ , attributable to  $\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})\text{H}$  (1917  $\text{cm}^{-1}$  in THF [16]). On removal of the solvent, the  $^1\text{H}$  NMR spectrum ( $\text{C}_6\text{D}_6$ ) of the crude product exhibited Cp resonances at  $\delta$  4.26 and 4.20 [16–21], indicating a ca. 1:1 ratio of  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$  and  $\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})\text{H}$ , and weak, unidentified Cp resonances at  $\delta$  4.48, 4.00 and 3.96. The methyl resonance of  $\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})\text{H}$  was observed at  $\delta$  1.28 (d,  $J_{PC}$  8.4 Hz), and additional doublet peaks were observed at  $\delta$  1.10 (d,  $J_{PH}$  7.61 Hz) and 0.97 (d,  $J_{PH}$  8.01 Hz). Hydride resonances were also observed at

$\delta$  – 12.8 (d, Fe–H of CpFe(CO)(PPh<sub>3</sub>)H), – 13.9 (d, Fe–H of CpFe(CO)(PMe<sub>2</sub>Ph)H) [22,23], – 13.34 (t) and – 14.32 (dd).

#### 2.1.5. Reaction of CpFe(CO)(PPh<sub>3</sub>)H with CO

A solution of 0.252 g ( $6.11 \times 10^{-4}$  mol) CpFe(CO)(PPh<sub>3</sub>)H in 20 ml benzene was wrapped in Al foil and CO was bubbled through the solution for 4.5 min. After the CO purge, a very strong band at 2015 cm<sup>-1</sup>, attributable to CpFe(CO)<sub>2</sub>H [21], was observed in the IR spectrum (the second band was obscured by a benzene band), and the intensity of the band of CpFe(CO)(PPh<sub>3</sub>)H (1925 cm<sup>-1</sup>) was reduced significantly. Significant decomposition of CpFe(CO)<sub>2</sub>H had not occurred after 2 h of stirring; a weak band at 1780 cm<sup>-1</sup> indicated only a small amount of decomposition to [CpFe(CO)<sub>2</sub>]<sub>2</sub> [23].

#### 2.1.6. Reaction of CpFe(CO)(PPh<sub>3</sub>)H with PMe<sub>2</sub>Ph

A solution of 0.20 g ( $4.86 \times 10^{-4}$  mol) CpFe(CO)(PPh<sub>3</sub>)H in benzene was treated with 86  $\mu$ l ( $6.04 \times 10^{-4}$  mol) PMe<sub>2</sub>Ph. Although there was little change in the IR spectrum after 5 h, a <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) spectrum of the reaction mixture exhibited the Cp resonances of CpFe(CO)(PPh<sub>3</sub>)H and CpFe(CO)(PMe<sub>2</sub>Ph)H, in a 2:1 ratio, at  $\delta$  4.25 (s, ) and 4.20 (d,  $J_{PC}$  1.6 Hz, [16–21]). The corresponding hydride resonances were observed at  $\delta$  – 12.8 (d, Fe–H) and – 13.9 (d, Fe–H) respectively.

### 2.2. Hydrogen atom abstraction reactions of CpFe(CO)(PMe<sub>2</sub>Ph)H

A solution of 0.1 g ( $2.0 \times 10^{-4}$  mol) trityl dimer in 10 ml of toluene was combined with 0.110 g ( $3.78 \times 10^{-4}$  mol) CpFe(CO)(PMe<sub>2</sub>Ph)H in 10 ml toluene ( $\nu_{CO}$  1918 cm<sup>-1</sup>). Within 10 min the solution changed from yellow to dark green, and the IR spectrum exhibited CO bands at 1919 (br), 1736, 1732 and 1692 cm<sup>-1</sup>. After 2 h, the IR spectrum of the green solution exhibited CO bands at 1919 (br), ~ 1930 (sh), 1736 and 1732 cm<sup>-1</sup>. The bands at ca. 1930 (sh), 1736 and 1732 cm<sup>-1</sup> are assigned to the di-iron complex Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>(PMe<sub>2</sub>Ph) ([16,17,22,23] see below).

#### 2.2.1. Reaction of CpFe(CO)(PMe<sub>2</sub>Ph)H with trityl in the presence of MeI

A solution of 0.24 g ( $8.33 \times 10^{-4}$  mol) CpFe(CO)(PMe<sub>2</sub>Ph)H in 10 ml benzene was treated with 161  $\mu$ l ( $2.59 \times 10^{-3}$  mol) MeI in 5 ml of benzene. The yellow solution turned green within 1 min, and an IR spectrum run at this time exhibited only a strong band at 1943 cm<sup>-1</sup>, attributed to CpFe(CO)(PMe<sub>2</sub>Ph)I (1938 cm<sup>-1</sup> in CHCl<sub>3</sub> [24]). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  d 3.94 (d,  $J_{PC}$  1.4 Hz, Cp), 1.73 (d,  $J_{PH}$  10.0 Hz, PMe), 1.43 (d,  $J_{PH}$  9.2 Hz, PMe).

#### 2.2.2. Reactions of CpFe(CO)(PMe<sub>2</sub>Ph)H with EtI and PhCH<sub>2</sub>Br

A solution of 0.075 g ( $2.6 \times 10^{-4}$  mol) CpFe(CO)(PMe<sub>2</sub>Ph)H in 10 ml of benzene was treated with 40  $\mu$ l ( $5.00 \times 10^{-4}$  mol) of EtI. The solution changed from yellow to dark green within 5 min and the reaction was complete within 30 min, at which time a strong band at 1943 cm<sup>-1</sup>, attributable to CpFe(CO)(PMe<sub>2</sub>Ph)I, was observed in the IR spectrum. Similar results were obtained with PhCH<sub>2</sub>Br, the solution changing from yellow to green within 1 min and the final product being identified as CpFe(CO)(PMe<sub>2</sub>Ph)Br. IR (benzene): 1946 cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  3.99 (s, Cp), 1.69 (d,  $J_{PH}$  10.4 Hz, PMe), 1.35 (d,  $J_{PH}$  9.6 Hz, PMe).

#### 2.2.3. Reaction of CpFe(CO)(PMe<sub>2</sub>Ph)H with trityl in the presence of *n*-BuCl

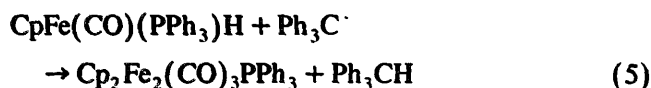
A solution of 0.17 g ( $5.90 \times 10^{-4}$  mol) CpFe(CO)(PMe<sub>2</sub>Ph)H and 91.5  $\mu$ l ( $8.76 \times 10^{-4}$  mol) *n*-BuCl in 16 ml benzene was treated with 0.86 g ( $1.77 \times 10^{-3}$  mol) trityl dimer in 50 ml benzene. An IR spectrum exhibited a strong broad band in the region 1932–1917 cm<sup>-1</sup>, a broad shoulder in the region 1889–1869 cm<sup>-1</sup>, and a bridging CO band at 1733 cm<sup>-1</sup>. After ca. 4.5 h, the solvent was removed and the residue was redissolved in CH<sub>2</sub>Cl<sub>2</sub>. IR (CH<sub>2</sub>Cl<sub>2</sub>): 1934 (m, br), 1736 (w), 1727 cm<sup>-1</sup> (w). Chromatographic separation of the reaction mixture was accomplished on a column packed with alumina and equilibrated with hexanes. Toluene as eluent removed a yellow solution containing no carbonyl species, diethyl ether a green band. Removal of ethyl ether solvent and redissolution in toluene showed this product, probably Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>PMe<sub>2</sub>Ph, to have strong bands at 1932 and 1734 cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.42–6.97 (m, Ph), 4.47 (Cp), 4.00, (d,  $J_{PH}$  1.6 Hz, Cp) and 0.93 (d,  $J_{PH}$  9.2 Hz, PMe). Repetition of this reaction in *n*-BuCl resulted in significant formation of CpFe(CO)(PMe<sub>2</sub>Ph)Cl ( $\nu_{CO}$  1951 cm<sup>-1</sup>; 1956 cm<sup>-1</sup> in hexadecane [18]). The assignment was confirmed by the reaction of CpFe(CO)(PMe<sub>2</sub>Ph)H with CCl<sub>4</sub>, which yielded green CpFe(CO)(PMe<sub>2</sub>Ph)Cl (IR 1956 cm<sup>-1</sup> in CCl<sub>4</sub>, 1952 cm<sup>-1</sup> in *n*-BuCl).

#### 2.2.4. Attempted reaction of CpFe(CO)(PMe<sub>2</sub>Ph)H with *n*-BuCl

A solution of 0.016 g ( $5.55 \times 10^{-5}$  mol) CpFe(CO)(PMe<sub>2</sub>Ph)H in 10 ml benzene was treated with 172  $\mu$ l ( $1.65 \times 10^{-3}$  mol) *n*-BuCl in 5 ml benzene. There was no reaction after 1 h (IR). The IR spectra recorded showed only the hydride band at 1916 cm<sup>-1</sup> with its 1870 cm<sup>-1</sup> shoulder. An additional 160 ml *n*-BuCl were added. Approximately 10 min later, the IR spectrum showed that the hydride was still the only carbonyl-containing product present.

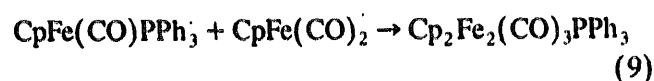
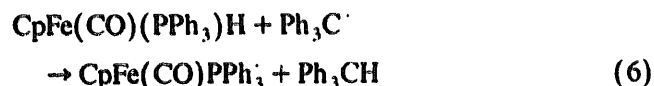
### 3. Results and discussion

Hydrogen atom abstraction from  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$  by the trityl radical yields the green, monosubstituted di-iron compound  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$  [16,17,22,23] and triphenylmethane (Eq. (5)).



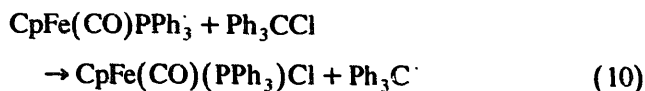
The IR spectrum of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$  in benzene exhibited a characteristic bridging carbonyl band at  $1732\text{ cm}^{-1}$ , in agreement with the literature [16,17,22,23]. In  $\text{CH}_2\text{Cl}_2$ , bands indicative of a mixture of cis and trans isomers in solution [16,17] were observed at 1950, 1772 and  $1723\text{ cm}^{-1}$ , comparing well with the IR spectrum of an authentic sample of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$  prepared via thermolysis of  $[\text{CpFe}(\text{CO})_2]_2$  in the presence of  $\text{PPh}_3$  [17]. With serendipity, solvated but analytically pure crystals of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$  were also obtained during a synthesis of  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$ . White [17] has reported that the compound  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$  is unstable over long periods of time as a solid, and decomposes within hours in solution at room temperature in the absence of excess phosphine. Such instability was not observed in these studies, although precautions were taken to purify and store the material at low temperatures.  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$  can also be synthesized photochemically via substitution of  $[\text{CpFe}(\text{CO})_2]_2$  with  $\text{PPh}_3$  [22,23].

Neither the radical  $\text{CpFe}(\text{CO})\text{PPh}_3$  nor the anticipated disubstituted dimer  $[\text{CpFe}(\text{CO})\text{PPh}_3]_2$  were observed in the final products. Dimerization was possibly inhibited because of steric constraints; but, it is nonetheless clear that the iron radical did form as a transient species, as hydrogen atom abstraction is implicit in the method employed, and the expected by-product, triphenylmethane, was observed. The formation of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$  is probably a consequence of coupling of the initially formed monosubstituted radical with the dicarbonyl radical,  $\text{CpFe}(\text{CO})_2\cdot$ , formed by substitution of  $\text{CpFe}(\text{CO})\text{PPh}_3$  by CO released during partial decomposition of  $\text{CpFe}(\text{CO})\text{PPh}_3$  (Eqs. (6)–(9)).



An analogous mechanism was proposed to explain the formation of the monosubstituted bimetallic species  $\text{Cp}_2\text{Mo}_2(\text{CO})_3\text{PPh}_3$  following hydrogen atom abstrac-

tion from  $\text{CpMo}(\text{CO})(\text{PPh}_3)\text{H}$  [3]. However, when the hydrogen abstraction reaction is carried out in the presence of unreduced  $\text{Ph}_3\text{CCl}$ , some  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{Cl}$  forms as a consequence of halogen abstraction from the organic halide (Eq. (10)).

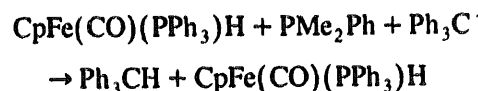


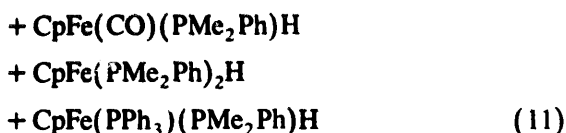
Similar reactions have been observed in other systems employing trityl radical solutions [3,8]. In this case, a control experiment demonstrated that the direct reaction of  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$  with  $\text{Ph}_3\text{CCl}$  to form  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{Cl}$  proceeds relatively slowly.

The chloro compound  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{Cl}$  was readily identified spectroscopically, and is also formed on hydrogen atom abstraction from  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$  by trityl in  $\text{CH}_2\text{Cl}_2$ . In the latter reaction, the source of the chlorine atom was the solvent.

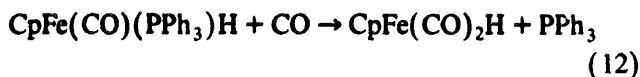
Complementing this work, it has been reported that while irradiation of  $[\text{CpFe}(\text{CO})_2]_2$  in the presence of 0.1 M  $\text{PPh}_3$  and 0.1 M  $\text{CCl}_4$  results in the formation of  $\text{CpFe}(\text{CO})_2\text{Cl}$  instead of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$ , use of 0.1 M  $n\text{-C}_5\text{H}_{11}\text{I}$  instead of  $\text{CCl}_4$  results in the formation of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$  as the major product, with only a minor amount of  $\text{CpFe}(\text{CO})_2\text{I}$  [23]. Thus the proclivity of metal-centered radicals to contemplate coupling rather than trapping pathways depends greatly on the relative efficiencies of the two processes.

To further illustrate that  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$  was the product of radical coupling, as in Eqs. (6)–(9), a reaction of  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$  with a deficiency of trityl was carried out in the presence of added  $\text{PMe}_2\text{Ph}$ . Substitution reactions of  $\text{CpFe}(\text{CO})_2\cdot$  with small phosphines are rapid [15], and it was anticipated that the added  $\text{PMe}_2\text{Ph}$  would intercept any  $\text{CpFe}(\text{CO})_2$  that might be generated. Certainly the dicarbonyl radical would react more readily with the small phosphine than with  $\text{CpFe}(\text{CO})\text{PPh}_3$ , thereby retarding the formation of the di-iron complex  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$ . Although a control experiment showed that direct substitution of  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$  with  $\text{PMe}_2\text{Ph}$  to form  $\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})\text{H}$  does occur relatively slowly, there was a significant increase in the amount of  $\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})\text{H}$  formed in the presence of trityl radical, approximately equal amounts of the two monosubstituted di-iron compounds being formed. Interestingly, weaker hydride resonances in the  $^1\text{H}$  NMR spectrum of the reaction mixture suggested that the bis(phosphine) hydrides  $\text{CpFe}(\text{PMe}_2\text{Ph})_2\text{H}$  ( $\delta -13.34$  (t)) and  $\text{CpFe}(\text{PMe}_2\text{Ph})(\text{PPh}_3)\text{H}$  ( $-14.32$  (dd)) were also formed (Eq. (11)), evidence for great lability in substituted iron radicals.





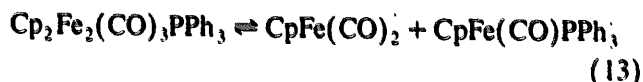
We wished to assess the role of free CO, suggested by Eq. (8), and it was anticipated that hydrogen abstraction in the presence of excess CO would increase the rate of formation of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$  by facilitating Eq. (12). However, it was found in a control experiment that  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$  undergoes rapid, direct substitution of  $\text{PPh}_3$  under a CO atmosphere to give  $\text{CpFe}(\text{CO})_2\text{H}$  (Eq. (12)).



Stabilization of  $\text{CpFe}(\text{CO})_2\text{H}$  with respect to decomposition to  $[\text{CpFe}(\text{CO})_2]_2$  by use of thiophenol and other additives has been described [21], but the similar use of CO has not been previously noted.

Although  $\text{CpFe}(\text{CO})\text{PPh}_3$  is not persistent and could not be isolated, the formation of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$ , the halide abstraction reactions observed, and the reactions with added phosphine provide conclusive evidence that  $\text{CpFe}(\text{CO})\text{PPh}_3$  had in fact been generated by hydrogen atom abstraction. Bogdan et al. [19] also found support for radical formation based on the production of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$ , among other products, in the reaction of  $\text{Mn}_2(\text{CO})_{10}$  with  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$ , thermally dissociated  $\text{Mn}(\text{CO})_5$  causing hydrogen atom abstraction from the iron hydride.

While the IR spectra of all samples of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$ , prepared via several routes, agreed with literature data for this compound, all of the samples prepared in this work exhibited a broad Cp resonance at  $\delta$  4.22 in  $\text{C}_6\text{D}_6$  ( $\delta$  4.16 in toluene- $d_8$ ), and we believe that the broadened singlet and the doublet at  $\delta$  4.57 and 4.52 which have previously been reported for this compound in toluene- $d_8$  [17] may be in error. As for the source of the broadening, it was initially thought that the broadening of the Cp resonance might arise from a di-iron compound-radical exchange (Eq. (13)), which would cause averaging of the cyclopentadienyl signals.

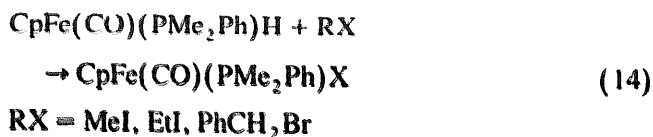


If such an equilibrium were involved, reaction of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$  with MeI would result in iodine atom abstraction by the two metal-centered radicals and the formation of some or all of the complexes  $\text{CpFe}(\text{CO})_2\text{I}$ ,  $\text{CpFe}(\text{CO})_2\text{Me}$ ,  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{I}$  and  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{Me}$  [1]. However, these products were not observed when  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$  was exposed to MeI for 4 h, and the dissociative equilibrium of Eq. (13) does not apply.

Instead, it seems likely that the broadened Cp signal observed in the NMR spectrum of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$  is an averaged resonance resulting from facile exchange of the four Cp rings of the cis and trans isomers of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$  [16,17].  $[\text{CpFe}(\text{CO})_2]_2$  has been reported to exist as cis and trans isomers in non-polar solvents, with less than 1% of an unbridged isomer [26,27]. A variable-temperature  $^1\text{H}$  NMR study of  $[\text{CpFe}(\text{CO})_2]_2$  has shown that the Cp singlet observed at room temperature for this compound decoalesces below 225 K to two resonances of essentially the same intensity at lower temperatures [27]. In a variable-temperature  $^1\text{H}$  NMR study of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$  in toluene- $d_8$  we similarly found that the broad Cp resonance at  $\delta$  ca. 4.2 at 298 K decoalesced to four distinct resonances at  $\delta$  3.83, 4.08, 4.27 and 4.41 between 270 and 298 K, the spectral changes being completely reversible. The temperature dependence of the  $^1\text{H}$  NMR spectrum of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$  is being investigated further.

Generation of  $\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})$  via hydrogen atom abstraction from  $\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})\text{H}$  with trityl dimer in benzene resulted in formation of the green di-iron compound  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PMe}_2\text{Ph}$ . The CO stretching bands of this compound, at ca. 1930, 1736 and  $1732\text{ cm}^{-1}$ , are similar to those of similar monophosphine di-iron complexes [16,17,22,23], and the presence of two bridging CO bands may imply the presence of cis and trans isomers [22,23]. In contrast to the broad Cp resonance observed for  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$ , the room temperature  $^1\text{H}$  NMR spectrum of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PMe}_2\text{Ph}$  exhibited two distinct Cp resonances at  $\delta$  4.00 (d,  $J_{\text{PH}}$  1.6 Hz) and 4.47 (s).

We had intended to carry out trityl hydrogen atom abstraction reactions of  $\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})\text{H}$  in the presence of organic halides, as described above with  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$ . It was anticipated that the organic halides would behave as radical traps, the anticipated iron-centered radical reacting as in Eq. (2). Unfortunately, a preliminary investigation showed that  $\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})\text{H}$  itself reacts rapidly with MeI, EtI and  $\text{PhCH}_2\text{Br}$  in benzene, even in the absence of trityl radical, forming  $\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})\text{I}$  [24] or  $\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})\text{Br}$  (cf.  $\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})\text{Cl}$ , IR:  $1956\text{ cm}^{-1}$  (hexadecane) [18]) (Eq. (14)), the anticipated products of the planned radical trapping experiments.



However  $\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})\text{H}$  was found not to react with *n*-butyl chloride, presumably because of its relatively high carbon-halogen bond strength [28], and we therefore assessed the possibility of using this alkyl halide as a trap for the  $\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})$  radical,

generated via trityl abstraction reactions with  $\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})\text{H}$ . Interestingly, the reaction of  $\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})\text{H}$  with trityl in the presence of *n*-butyl chloride in benzene resulted in the formation only of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PMe}_2\text{Ph}$ , identified spectroscopically. Clearly ligand rearrangement and coupling of the metal-centered radicals so generated (Eqs. (6)–(9)) was far more favorable than halogen abstraction from *n*-butyl chloride. However, hydrogen atom abstraction from  $\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})\text{H}$  conducted in *n*-butyl chloride as solvent did result in the formation of  $\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})\text{Cl}$ .

During the course of the reaction in *n*-butyl chloride, an ephemeral band was observed at  $1910\text{cm}^{-1}$ , very similar to the CO bands of  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{Me}$  ( $1905\text{cm}^{-1}$  in  $\text{CHCl}_3$  [24]). On this basis, the intermediate is tentatively suggested to be  $\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})(n\text{-Bu})$  formed by coupling of  $\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})$  and the *n*-butyl radical and possibly providing further evidence for chlorine atom abstraction from *n*-butyl chloride by  $\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})$ .

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